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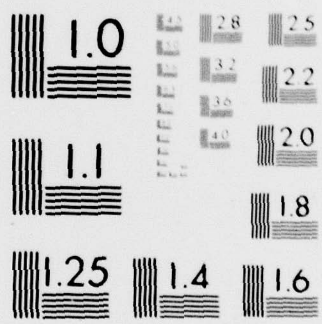
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FINAL TECHNICAL REPORT

on

INFLUENCE OF STOICHIOMETRY ON IMPINGEMENT EROSION OF LEAD SULFIDE AND ZINC SELENIDE

to

AIR FORCE OFFICE OF SCIENTIFIC RESEARCH

by

R. G. Hoagland and I. G. Wright

AFOSR-77-3283

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The results of a series of water droplet impingement erosion experiments on lead sulfide and zinc selenide are described. The work with single crystal lead sulfide sought to correlate the mechanisms of surface damage with mechanical strength, lead sulfide affording an opportunity to study the effect of a range of hardness, caused by a shift in stoichiometry into the p-type range, in specimens otherwise similar in elastic properties and pre-existing dislocation substructures. Dislocations involved in the deformation resulting from water droplet impacts were revealed by etch pitting. (Cont'd on reverse side)

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The size and nature of the impact sites on all the lead sulfide specimens studied, using 0.42 mm water droplets impacting at 100-168 m/s, was found to be in fact highly stochastic. The deformation produced was strongly dependent upon the pre-existing arrangement of dislocations at the impact site, and considerable effort was expended in obtaining suitably dislocation-free crystal surfaces. Because of the relatively small number of dislocations extant and the short duration of the pressure loading from impacts, hardness increases obtained by doping did not significantly affect the material response to single impacts.

The polycrystalline zinc selenide examined is a prime candidate material for windows for IR imaging devices. Although etch pitting could not be employed to reveal deformation, the initiation and propagation of damage was studied as a function of time (for multiple impacts) by conventional surface examination techniques. The grain boundaries in this material appeared to act as flaw sites which, upon repeated impact, led to the encirclement of complete grains by cracks, with consequent material loss.

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ABSTRACT

The results of a series of water droplet impingement erosion experiments on lead sulfide and zinc selenide are described. The work with single crystal lead sulfide sought to correlate the mechanisms of surface damage with mechanical strength, lead sulfide affording an opportunity to study the effect of a range of hardness, caused by a shift in stoichiometry into the p-type range, in specimens otherwise similar in elastic properties and pre-existing dislocation substructures. Dislocations involved in the deformation resulting from water droplet impacts were revealed by etch pitting. The size and nature of the impact sites on all the lead sulfide specimens studied, using 0.42 mm water droplets impacting at 100-168 m/s, was found to be in fact highly stochastic. The deformation produced was strongly dependent upon the pre-existing arrangement of dislocations at the impact site, and considerable effort was expended in obtaining suitably dislocation-free crystal surfaces. Because of the relatively small number of dislocations extant and the short duration of the pressure loading from impacts, hardness increases obtained by doping did not significantly affect the material response to single impacts.

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from

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Columbus Laboratories

INTRODUCTION

This program was conceived to explore the potential improvements in impingement erosion resistance which might be realized through modification of mechanical properties of deformable solids. The lack of information correlating the mechanisms of surface damage and removal with mechanical strength made it difficult to assess the consequences of such modification, a priori. Consequently, the objectives of this program were to investigate in detail the mechanisms of surface layer deformation during impingement erosion.

In this study the impacts were produced by water droplets with a controlled diameter and impact velocity. The impacts were produced on two materials: single crystal lead sulfide and polycrystalline zinc selenide. The former material is a semiconductor with mechanical properties quite similar to those possessed by IR-transparent materials which are currently candidates for various IR imaging devices operating under water droplet erosion conditions. Furthermore, lead sulfide offered a special advantage to this study as it can be chemically etched to reveal surface dislocations.

The resulting etch pit patterns provide a highly detailed map of the deformation occurring as a result of a droplet impact. Finally, PbS can be hardened by shifting the stoichiometry, with the largest effects appearing in the p-type range (excess sulfur). This capability permits strength increases without significant changes in elastic properties, density, or initial dislocation substructure.

The polycrystalline ZnSe examined in this program is a prime candidate IR window material. While deformation can not be revealed by etch pitting techniques in this material, it affords a useful vehicle for relating the generation of flaws to microstructure during impingement erosion of polycrystalline aggregates.

The major findings of this program indicate that within the range of impact conditions produced by 0.42 mm droplets impacting at 100 to 168 m/s, the nature of deformation at the impact site is determined primarily by the initial dislocation substructure at that location. Therefore, because the preexisting dislocation arrangements vary in a random fashion on a microscopic scale, the size of the damage zones are observed to be highly stochastic. In addition, in polycrystalline ZnSe the grain boundaries act as flaw sites and under repeated impacts, the encirclement of grains by cracks leads to material removal. These and other observations are described in greater detail below.

EXPERIMENTAL DETAILS

The experiments were conducted in Battelle's rotating arm apparatus described previously[1]. The arm and liquid droplet supply are housed within a vacuum chamber while the drive motor, spindle and bearings are outside the chamber and attached to its floor. The rotating shaft passes through a specially designed vacuum seal capable of maintaining moderate vacuum under conditions of high rotational speeds. Earlier versions of this system, employing a commercially available rotary vacuum feed-through and bearings, posed severe problems and the redesign of the drive system caused a serious eight-month delay in the first year of the program.

Water droplets are produced from the controlled pinch-off of a stream coming from an oscillating hypodermic needle. The flow rate and vibrational frequency can be adjusted to introduce a periodic instability in the stream which leads to droplets whose size can be controlled with great precision. All of the droplets used in this study had a diameter of 0.42 mm. During impingement the pressure was maintained at 20 mm Hg, the vapor pressure of water at 295 K (22 C). At this pressure, boiling of the droplets was prevented and breakup or distortion of the droplets by turbulence around the moving arm was minimized.

The PbS specimens were cleaved from single crystals grown by the Bridgman method. In most crystals, the subgrain size was so small that the crystals could not be cleaved without introducing regions of high dislocation density on the surfaces. Because these dislocations prevented the identification of any subsequent deformation, it was necessary to develop a mechanical-chemical polishing method to remove the deformed surface layers. Prior to an impingement run, each specimen was then etched and the surface was completely photographed at about 100X to map the initial dislocation distribution so that any subsequent deformation could be readily identified. The dimension of the samples was typically 4 x 6 x 5 mm. Sulfur doping pushing the stoichiometry into the p-type range was conducted in enclosed capsules containing sulfur which were heated to the temperature necessary to produce the desired sulfur pressure.

The polycrystalline ZnSe was obtained from Wright-Patterson AFB, courtesy of Tim Peterson. This material had a mixed grain size with grain diameters ranging from 2 μm to 50 μm. The impingement experiments on this material focused on characterizing multiple impact damage and the development of damage was followed through photomicrographs of specific areas at various times during the accumulation of impacts.

SUMMARY OF RESULTS

Approximately 500 single impacts were produced on single crystal PbS, with most of the impacts at about 168 m/s. The most characteristic feature of the results is the stochastic nature of the damage. This observation is demonstrated in Figure 1, which is a log-normal distribution plot of damage zone diameters derived from the average of two orthogonal measurements of the maximum extent of the dislocation rosette pattern at each impact

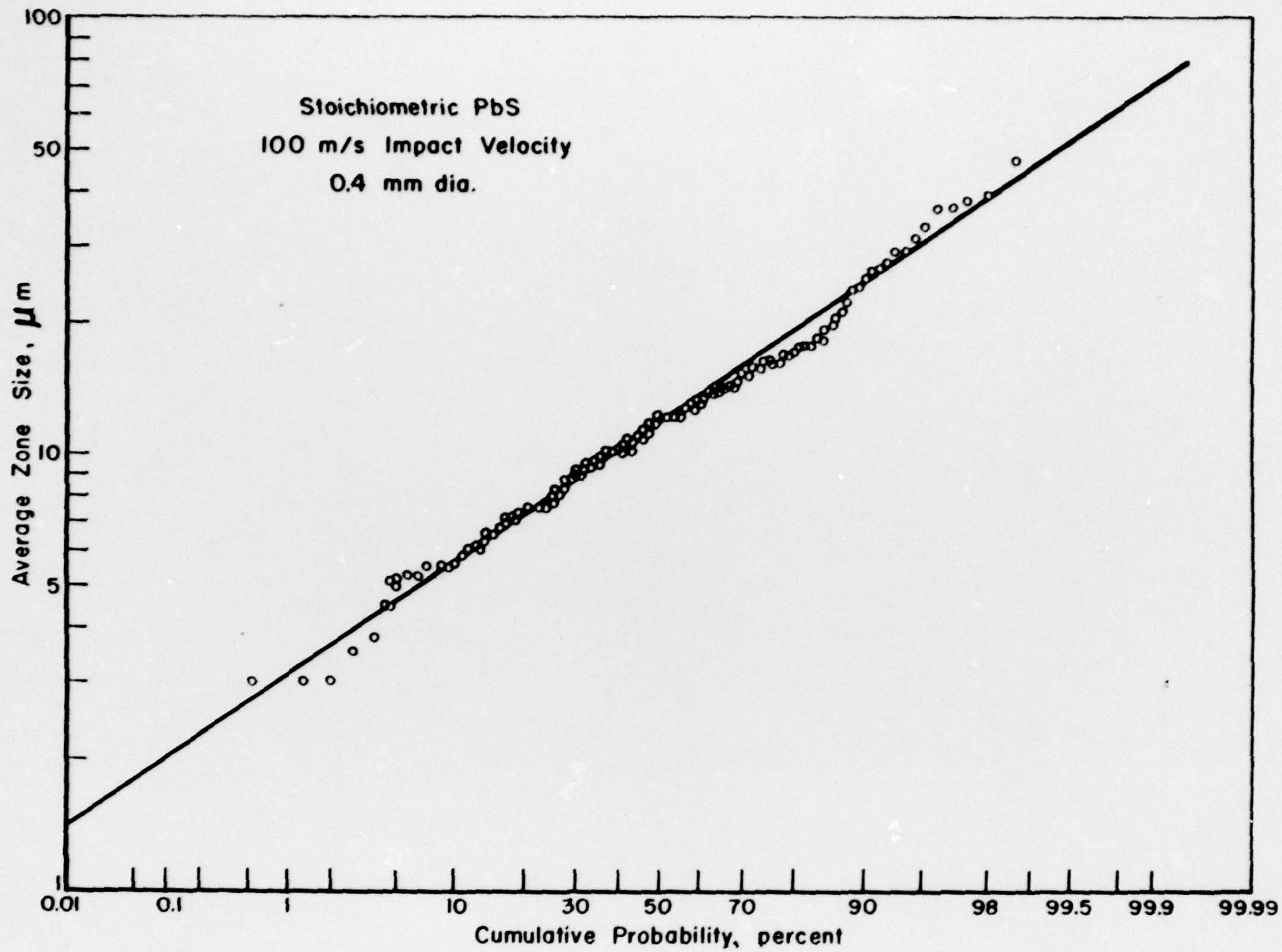


FIGURE 1. LOG-NORMAL CUMULATIVE PROBABILITY DISTRIBUTION OF DAMAGE-ZONE SIZES FOR IMPACT OF 0.42 mm DIAMETER WATER DROPLETS AT 100 m/s ON STOICHIOMETRIC PbS

Accuracy of size measurements estimated at $\pm$ 0.001 mm.

site. These measurements, shown here for 100 m/s impacts, were typical of those for stoichiometric and p-type PbS at 100 m/s and 168 m/s, and illustrate the large spread in damage-zone sizes observed.

Figure 2 shows examples of dislocation arrays reflecting the deformation produced by 0.42 mm diameter water droplets on stoichiometric PbS, and Figure 3 shows damage produced on PbS containing 2×10^{19} S atoms/cm^3. The significance of these damage arrangements may become clearer when they are compared to the ring-shaped depression produced by a 168 m/s impact on polymethylmethacrylate in Figure 4. This is the expected response of a homogeneous plastic material. Calculations show that the pressure distribution over the circular contact area during impact by a spherical drop is a maximum at the contact boundary and minimum at the center of contact(1,2). As the contact area grows the pressure at the boundary continues to increase until the rate of expansion of the contact zone becomes less than the sound velocity in the water. This occurs when the radius of the contact area is

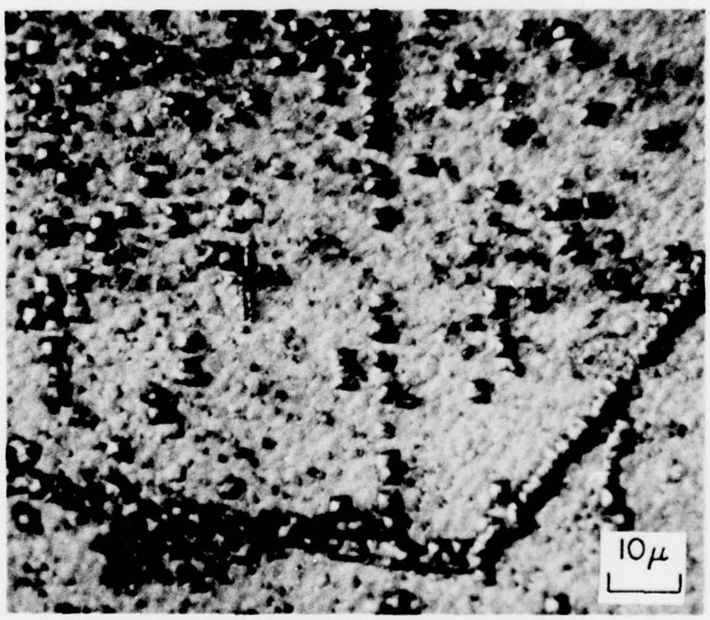
$$r_c = R\left(1 + \frac{C^2}{V^2}\right)^{-1/2} \tag{1}$$

where R is the droplet radius, C the sound velocity and V the impact velocity. For a 168 m/s impact of a 0.42 mm water droplet Equation (1) predicts a 23 μm radius (taking C = 1500 m/s). The peak pressure attained at the boundary of the contact area when the contact radius achieves the dimensions given by Equation 1 can be empirically derived from the results of Rosenblatt et al(2) and is given as

$$P_{max} = 2pCV\left(1 + \frac{2V}{C}\right) \tag{2}$$

where p is the density of water. As an example at 168 m/s impact velocity Equation (2) predicts $P_{max} = 7.4 \times 10^8$ Pa (107.7 ksi). This pressure is considerably greater than the flow stress of either PbS or PMMA and therefore plastic deformation of these materials is expected. After this radius has been reached the normal pressure should fall precipitously and therefore the depression in Figure 4, which has an 18 μm radius, is consistent with these predictions.

(a)

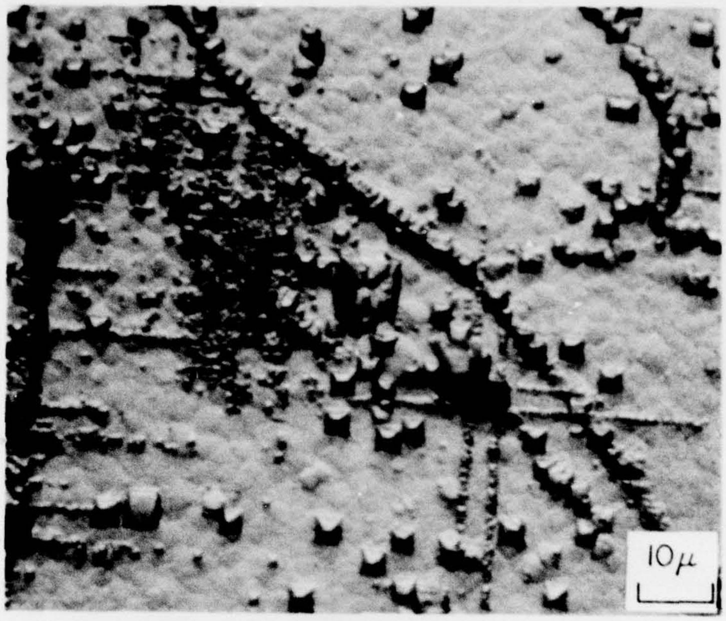


(b)

FIGURE 2. EXAMPLES OF DISLOCATION ARRAYS PRODUCED IN STOICHIOMETRIC PbS, BY 0.42 mm WATER DROPLETS AT 168 m/s

(a) Impact site rosette with damage partially attenuated by interaction with preexisting dislocation (~40 impacts/mm^2)

(b) Small impact site (~40 impacts/mm^2)



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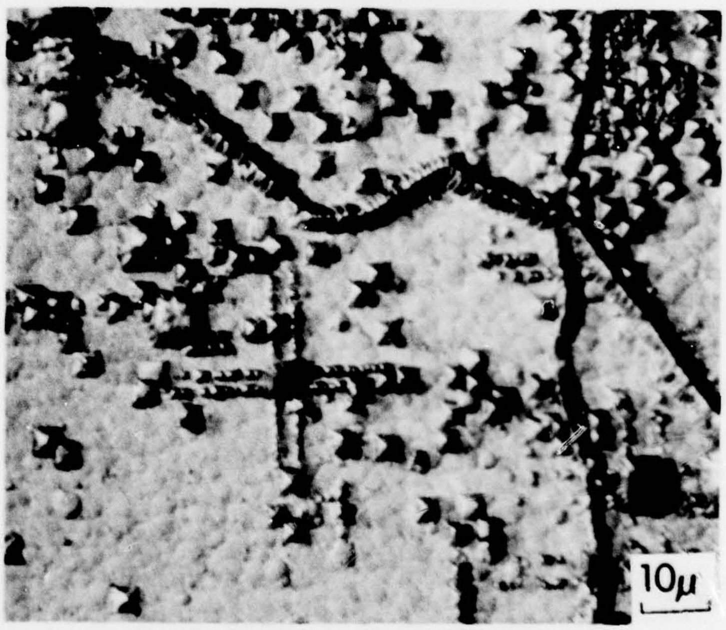

(b)

FIGURE 3. IMPACT SITES IN p-TYPE PbS, 0.42 mm WATER DROPLETS AT 168 m/s SHOWING

(a) Interaction of impacts (very fine etch pits) with preexisting dislocations (~40 impacts/mm^2)

(b) Interaction with large flat-bottomed etch pits (~40 impacts/mm^2)

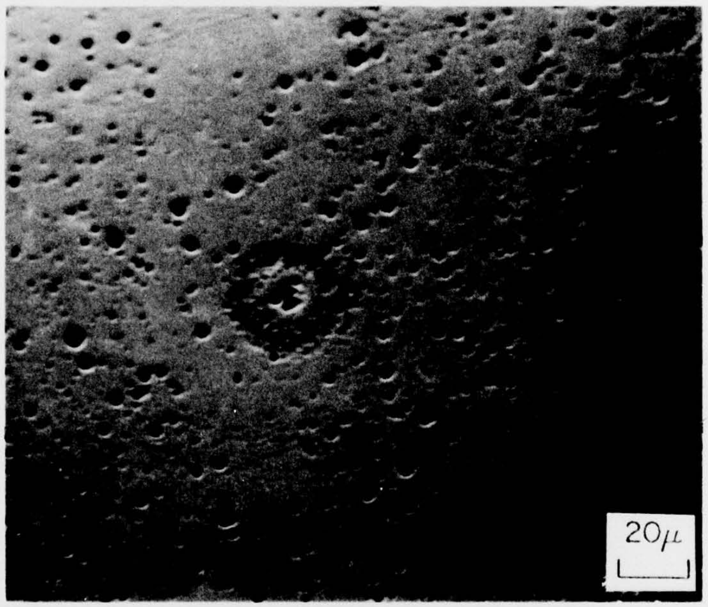

FIGURE 4. IMPACT SITE IN POLYMETHYLMETHACRYLATE (PMMA) BY A WATER DROPLET OF 0.42 mm DIAMETER AT 168 m/s

In PbS the deformation is accomplished via the creation and glide of <110> {100} dislocations. In our samples the initial dislocation density is on the order of 1×10^6 cm^{-2} which means that the average spacing between dislocations is about 10 μm*. As a consequence, for a 168 m/s impact by a 0.42 mm water droplet, Equation (1) suggests that (on average) about only 17 dislocations will be within the contact boundary at peak pressure. Furthermore, for these impact conditions the peak pressure is reached in only 7 nsec. It becomes clear then that both the time for operation of dislocation sources and the number of available sources are extremely limited. We are therefore led to the conclusion that the nature of the deformation introduced by an impact event will depend much more on the initial dislocation arrangement at the impact site than on the pressure distribution. It is in fact conceivable that an impact in a region devoid of dislocations would leave no irrecoverable deformation even though the bulk flow strength was exceeded by a considerable amount. The random distribution of dislocations accounts for the highly variable damage zone sizes and shapes.

As the observations of impact damage on stoichiometric PbS were made and analyzed, it became clear that the bulk flow properties would not be an indication of erosion resistance. This reasoning derives from the fact that the flow strength is a consequence of the response of a very large number of dislocations to a macroscopic stress field applied for a relatively long time. None of these conditions is met during water droplet impact. Consequently, the likelihood of substantially affecting erosion resistance by altering the flow strength appeared poor. This was indeed found to be the case since the impact damage on the sulfur-doped, p-type PbS was essentially indistinguishable from the stoichiometric PbS. This result occurred even though the sulfur doping to 2×10^{19} S atoms/cm^3 produces a hardness increase of 17%[(3)].

In Figure 5 are examples of the progression of damage on a multiply-impacted surface of ZnSe. The damage becomes evident as holes and pits where material is removed, as can be readily observed through examination of the progressive development of features such as those indicated as A and B in Figure 5. However, upon etching, considerably more damage is revealed in

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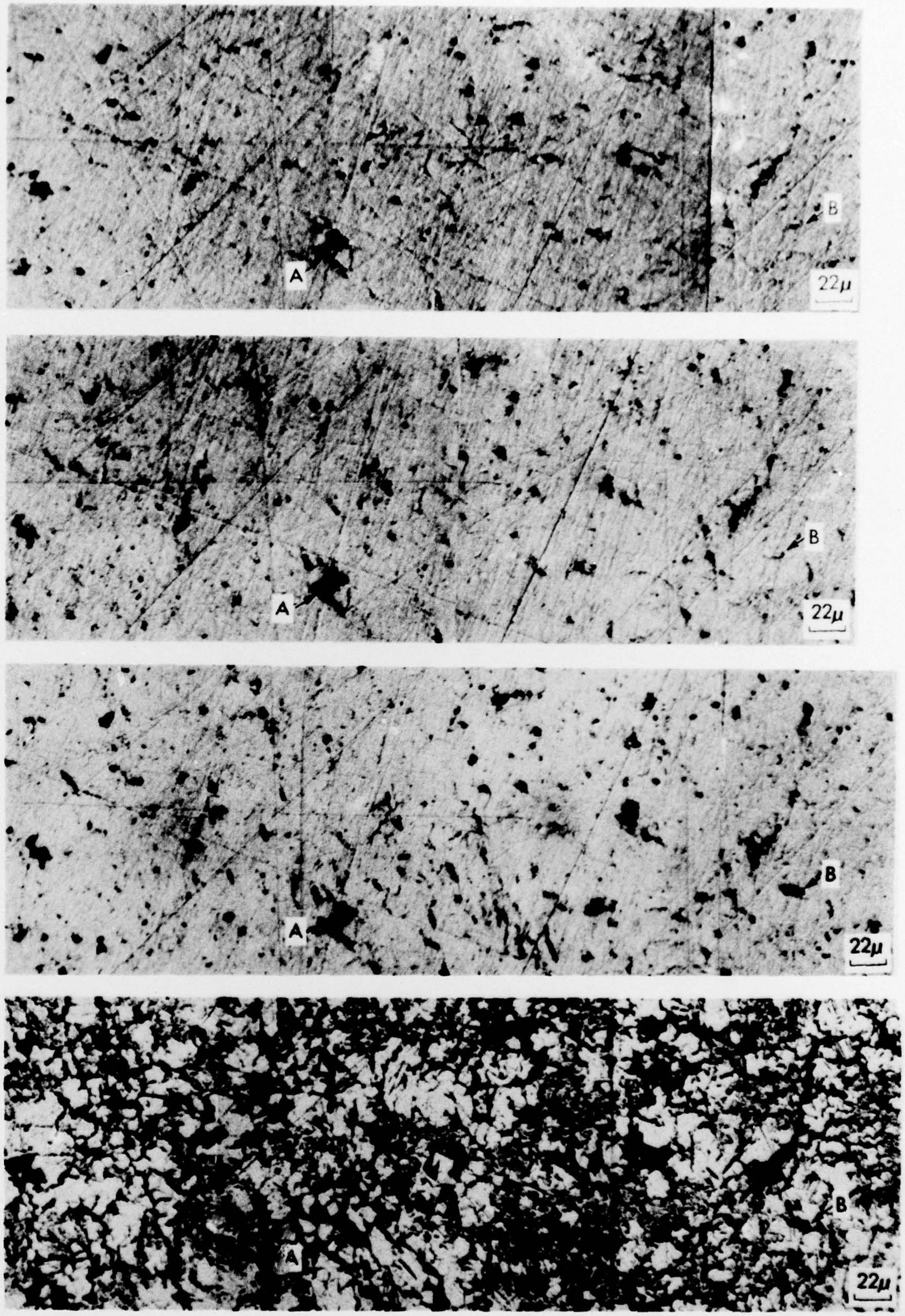
* This estimate excludes the dislocations contained in the low-angle boundaries.



(a) After 7 min. (~1.8 x 10^4 impacts/ mm^2)

(b) After 9 min. (~2.3 x 10^4 impacts/ mm^2)

(c) After 13 min. (~3.3 x 10^4 impacts/ mm^2)

(d) After 13 min., etched

FIGURE 5. SURFACE FEATURES OF FINE-GRAINED ZINC SELENIDE, SHOWING PROGRESSION OF DAMAGE WITH EXPOSURE TIME TO WATER DROPLETS OF 0.42 mm DIAMETER, AT 168 m/s

the form of a network of microcracks lying primarily along the grain boundaries, Figure 5d. These cracks are so tightly closed that they are not readily apparent in the unetched surface, but may be discerned by examination at high magnification in a scanning electron microscope, as shown in Figure 6, where the features A and B correspond to those observed optically in Figure 5. The formation of holes and pits appears to be a consequence of the complete encirclement of large grains by the microcracks, as can be seen in areas B and C in Figure 6. The formation of large craters as at C probably results from localization of hydraulic pressure when a small grain boundary chip becomes filled with liquid during a subsequent impact.

There are two possible sources for these microcracks. (1) The grain boundaries have a significantly lower surface energy (and, therefore, fracture toughness) or higher flaw density than the grains themselves, or (2) the stresses within the solid during impact are higher on the grain boundaries due to elastic anisotropy and incompatibility between neighboring grains. At this time it is difficult to identify which of the possibilities is correct.

CONCLUSIONS

(1) While the pressure distribution generated on a solid surface during impact by a spherical water droplet is a predictable spatial and temporal quantity, the plastic response of a crystalline material may not be predictable. The observations of deformation produced on single crystal PbS after impacts with 0.42 mm diameter water droplets show a tremendous variability. This variability is a consequence of the fact that the deformation produced during an impact is most strongly related to the initial dislocation arrangement at that impact site.

(2) Because the number of dislocations initially involved in impacts, for the conditions employed in this study, is quite small and the duration of the pressure loading is very short, the bulk flow properties do not adequately reflect erosion response. As a consequence, hardness increases by sulfur doping PbS did not materially affect the nature of single impact deformation.

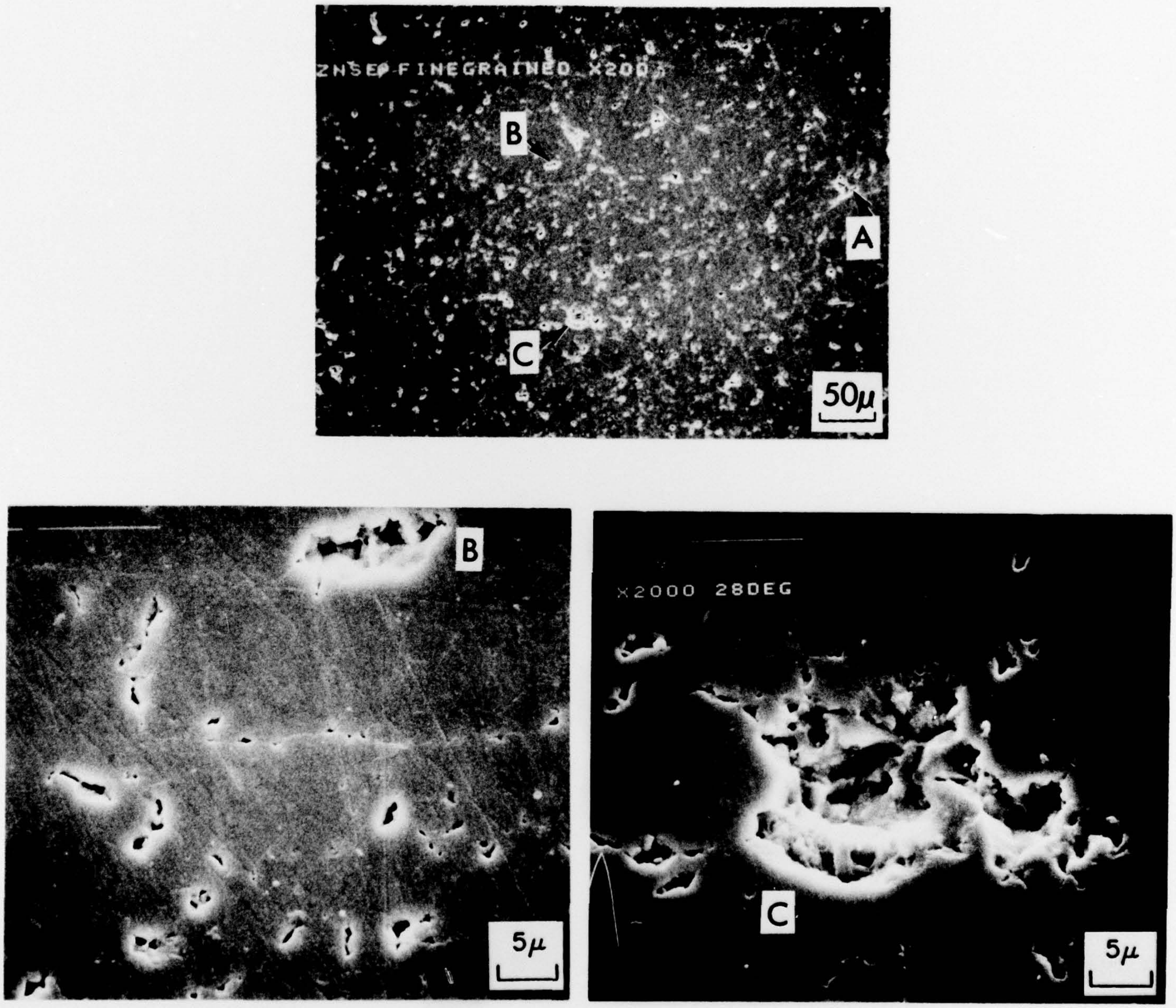


FIGURE 6. SCANNING ELECTRON MICROGRAPHS OF SURFACE DAMAGE PRODUCED IN FINE-GRAINED ZnSe BY 0.42 mm WATER DROPLETS AT 168 m/s, AFTER 13 MINUTES EXPOSURE (3.3 x 10^4 IMPACTS/mm^2)

Top: General view of surface, with three areas of interest identified.

Bottom: Details of areas B and C, showing the very fine, tight cracks produced, and the apparent relationship with grain boundaries.

(3) In polycrystalline ZnSe, material removal under multiple-impact conditions occurs by the encirclement of grains by grain boundary microcracks.

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